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Numerical evaluation of energy shifts due to dipole moments interaction in a hydrogen atom

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Abstract

This study aimed to numerically investigate the impact of dipole-dipole interactions on the energy levels of a hydrogen atom, specifically the energy shift caused by the interaction of the atom's dipole moment with external electric fields. This research involved applying perturbation theory and numerical techniques to quantify the changes in energy levels due to dipole orientations and magnitudes, contributing to a deeper understanding of atomic behavior and its implications in various scientific disciplines. The results presented showed that the wavefunction of the hydrogen atom exhibits degeneracy, especially $n = 2$, $n = 3$ states. This implies that $n = 2$, $n = 3$, have different states but the same energy as a result of the subshells with angular momentum l, which contains $2l+1$ distinct state corresponding to positive value of m (magnetic angular momentum quantum number) $m = -l \pm 1$. The total degeneracy of the energy levels n is caused by n^2. We find out that as the orientation of the electron charges (θ, ϕ) change the dipole moment also changes and thus has a perturbing effect on the energy levels of the hydrogen atom leading to a shift in its energy. This is confirmed, as the energy shift increases slightly from the ground state energy function Φ_{100} to the second exicted state Φ_{300}, while the degeneracy state of Φ_{310} experiences infinitesimal energy shift above. This is because the probability of the electron been found in the lower energy level is greater than at higher energy level and so it is mostly affected there by energy shift. Also, the dipole moment could increase liberational energy of the atom and thus lead to more excitement even though its impact is quite negative. The outcome of this study could have implications in precision measurements, quantum computing, and the understanding of complex atomic systems.

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1. Introduction

Studying the numerical evaluation of energy shifts resulting from dipole moment interactions within a hydrogen atom holds paramount importance in quantum physics by understanding fine details of atomic behavior, shedding light on the atom's internal dynamics. Such investigations contribute to refining quantum mechanical models, improving accuracy in atomic spectroscopy, and advancing fields like quantum computing and precision measurement. The rationale for the numerical evaluation of energy shifts

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due to dipole moment interactions in a hydrogen atom is primarily the need for accuracy in complex scenarios and the limitations of analytical methods, while the implications include a deeper understanding of intermolecular forces, spectral line shifts, and the validation of theoretical models in practical applications. The evaluation of these shifts in energy levels is fundamental for understanding atomic and molecular behavior, contributing to various equation fields such as quantum physics, spectroscopy, and atomic structure studies [1]. Moreover, comprehending these energy shifts aid in predicting and manipulating atomic properties, influencing diverse scientific disciplines, including material science, chemistry, and fundamental physics, thereby paving the way for technological advancements and a deeper understanding of the universe's building blocks. In quantum mechanics, dipole moments can cause perturbations in the atom's energy states, leading to shifts in the spectral lines [2].

The behavior of the dipole electronic properties of a hydrogen atom located half the distance between two impenetrable parallel planes is studied as a function of the inter-plane separation using the energies and wave functions reported previously in Ref. [3]. It was found that as the inter-plane separation is reduced, all the electronic properties are affected by the shifting of the electronic spectra towards the short wave-length region (EUV) with a boost of the photo-luminosity intensity, which followed that fluid temperature trend decreases with increase in magnetic field applied to perturbation state in reverse effect when radiation and unsteadiness was high [4], reduction of the static polarizability and life-time of the $2s$ and $2p$ states, increase of the mean excitation energy in conjunction with bound states in Coulombic field [5], and transition rates for characteristic plane separations wave functions are generalizations of the Coulomb field charges via dipole moment [6].

A hydrogen atom in its ground state has no permanent electric dipole moment due to the spherical symmetry of its electron cloud. Therefore, there is no static energy shift from a permanent dipole-dipole interaction for an isolated hydrogen atom or an ensemble of ground-state hydrogen atoms in a typical environment. However, energy shifts can arise from induced dipole moments and fluctuation-induced dipole moments [7] when a hydrogen atom interacts with an external electric field. When two neutral ground-state hydrogen atoms interact at large distances, the dominant force is the instantaneous dipole-induced-dipole interaction [8].

This interaction energy scales as $U \propto -\frac{1}{r^6}$ (where r is the atomic distance) leads to a slight attractive energy shift. The numerical value of this energy shift depends heavily on the distance (r) between the atoms. The interaction energy for two hydrogen atoms in their ground states is often described by a potential energy curve (e.g., in the hydrogen molecule formation), where the energy minimum (bond formation) is on the order of electron volts (eV), while the dispersion forces at larger distances are much weaker [9]. If a hydrogen atom is placed in an external electric field (E), an electric dipole moment is induced, leading to a Stark shift [10]. The energy shift is proportional to the square of the electric field (E^2) and the atom's polarizability (α). The typical energy shift values in standard laboratory fields are small compared to the atom's main energy levels (which are on the order of 10 eV). Relativistic and quantum electrodynamics (QED) effects cause a very small but measurable energy shift between the $2s_{1/2}$ and $2p_{1/2}$ states, known as the Lamb shift [11]. This is an internal atomic effect, not an interaction between separate dipole moments. Its numerical value is approximately 1057 MHz in frequency units.

Studies have shown theoretically that the dipole moment and its derivative with respect to H_2 internuclear distance were calculated for H_2–H_2 and H_2–H collisions in the adiabatic approximation [12, 13]. A conventional quantum mechanics in which the potential function is not specified but replaced by specifying four parameters Wilson-Racah orthogonal polynomials in the energy and physical parameter space was presented and the models give good approximate prediction of the Hydrogen atom energy with an estimated average error of 0.125% when used in determining the role of intermolecular interactions which can significantly modify optical responses and are quantified through interaction-induced properties [14, 15].

The dispersion interaction between two ground-state hydrogen atoms, interacting with the quantum electromagnetic field in the vacuum state, in presence of an external static electric field, both in the nonretarded and in the retarded Casimir-Polder regime was presented in Ref. [16]. The presence of external field strongly modifies the dispersion interaction between atoms, changing its space dependence and it was found that, for specific geometric configurations of the two atoms with respect to the external field, it is possible to change the character of the dispersion force, turning it from attractive, or even make it vanishing.

The energy shift in molecular spectra due to interaction of the nuclear magnetic quadrupole moment (M) with electrons is equal to $\delta E_M = MW_M P_M$, where W_M is a constant determined by the electronic structure of the molecule and P_M is a dimensionless constant was extended by the method of parity and non-conservation effects in triatomic molecules developed [17]. Results of the calculations are required for extraction of the M value from the YbOH (Ytterbium Monohydroxide) experiment.

Monitoring changes in molecular dipole moments through molecular dynamics simulations provides valuable insights into dipole–dipole interactions, which are critical for understanding protein structure stability and predicting protein–ligand binding affinity [18]. A novel method to monitor changes in the interangle between dipole vectors of residue molecules within proteins and ligand molecules, aiming to evaluate the strength and consistency of interactions within the complex was studied and the dipole moment analysis approach provides valuable predictive insights into complex candidates, especially in situations where experimental comparisons are challenging.

The molecular enhancement for the relevant symmetry-violating interaction in molecules, such as P, T-violating electron /electric dipole moment W_d, scalar-pseudoscalar nucleon-electron interaction W_s, and nuclear magnetic quadrupole moment W_M, and for the nuclear-spin-dependent P-violating anapole moment W_A was calculated in Ref. [19]. The relativistic four-component coupled-cluster method and systematic study to estimate the associated uncertainties in the approach was carried out. It was found that the individual contribution of each computational parameter to the total uncertainty in a system is approximately the same for all the calculated enhancement factors, summing up to a total uncertainty of $\sim 6\%$.

In the literatures so far surveyed, lots of works have been done on the energy shift caused by the interaction of the atom's dipole moment with external fields and the approaches are mainly weak, temporary attractive forces that exist between all atoms and molecules, caused by the constant motion of electrons creating temporary dipoles. Therefore, there is no static energy shift from a permanent dipole-dipole interaction for an isolated hydrogen atom or an ensemble of ground-state hydrogen atoms in a typical environment. This means that energy shifts can arise from induced dipole moments and fluctuation-induced dipole moments. Very little attention has been given to the fundamental fact that when a hydrogen atom interacts with an external electric field, a nearby atom/molecule, or an electron's potential is influenced due to relativistic effects. Specifically, we shall investigate the energy shift caused by the interaction of the atom's dipole moment with external electric fields by applying perturbation theory and numerical techniques to quantify the changes in energy levels due to dipole orientations and magnitudes, contributing to a deeper understanding of atomic behavior and its implications in various scientific disciplines.

2. Theoretical framework

2.1. Hydrogen-like wave function equations

The hydrogen-like wavefunction for other atoms with a single valence electron, such as He^+, Li_2^+, and Be_3^+ can be obtained by replacing the charge of the nucleus (Z) in the Coulomb wavefunction with the effective nuclear charge ($Z' = Z - \sigma$), where σ is a screening constant that takes into account the shielding effect of inner electrons. This results in a similar wavefunction with different values for A and n.

The hydrogen-like wavefunction is important in understanding the properties and behavior of atoms with single valence electrons, such as their energy levels, ionization energies, and chemical reactivity. It also provides a basis for understanding more complex atoms with multiple valence electrons through molecular orbital theory. Base on the theoretical background according to Ref. [2], the total wave functions are given by

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r)\, Y_l^m(\theta,\phi), \tag{1}$$

$$\psi_{nlm}(r,\theta,\phi) = \sqrt{\left(\frac{2}{an}\right)^3 \frac{(n-l-1)!}{2n\,[(n+l)!]^3}}\left(e^{-r/an}\right)\left(\frac{2r}{an}\right)^l \left[L_{n-l-1}^{2l+1}\left(\frac{2r}{an}\right)\right] Y_l^m(\theta,\phi). \tag{2}$$

where $L_{n-l-1}^{2l+1}\left(\frac{2r}{an}\right)$ are the Associate Laguerre polynomials defined by

$$L_n^k(x) = \frac{e^x x^{-k}}{n!}\frac{d^n}{dx^n}\left(e^{-x}x^{n+k}\right). \tag{3}$$

The angular part of the wave function is given by

$$Y_l^m(\theta,\phi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_{l,m}(\cos\cos\theta)\, e^{im\phi}, \quad m > 0, \tag{4}$$

with $P_{l,m}(\cos\cos\theta)$ as the Legendre polynomials. The wave functions for the hydrogen atom for $n = 1, 2, 3$ are presented in Table 1.

2.2. Energy shift in Hydrogen-like atom due to dipole moment

The energy shift in a hydrogen atom due to its dipole moment is a small perturbation to the energy levels caused by the interaction between the electric dipole moment of the atom and an external electric field. This effect is known as the Stark effect. The dipole moment of a hydrogen atom is very small, as the electron and proton have opposite charges and are bound together by the Coulomb force. However, in an external electric field, this dipole moment can induce a small energy shift in the hydrogen atom's energy levels. The first order correction to energy for the different wave functions of the hydrogen-like atom is used to determine the energy shift caused by the effect of the dipole moment. Again, according to Ref. [2];

$$E_n = E_n^{(0)} + E_n^{(1)}, \tag{5}$$

$$E_n^{(0)} = -\frac{R}{n^2}, \tag{6}$$

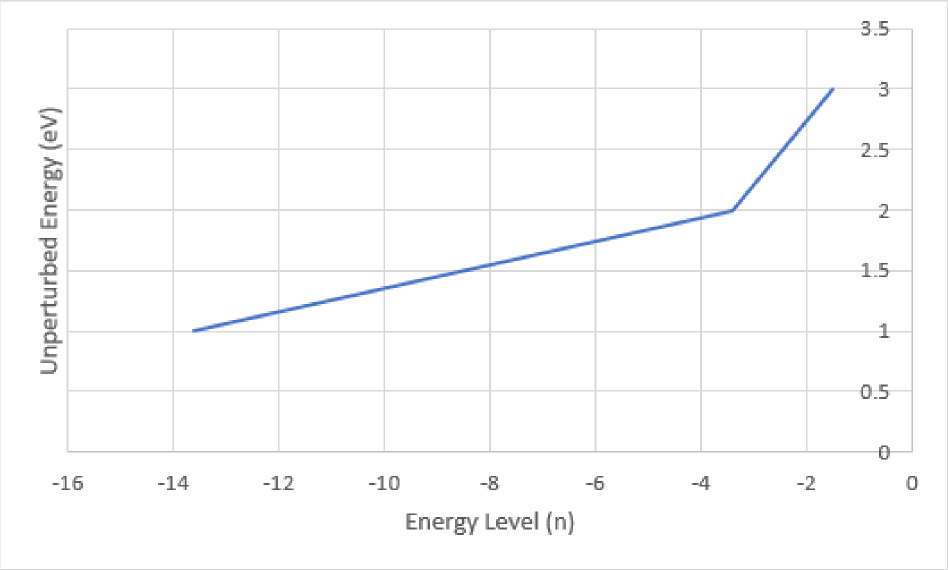

Figure 1. Unperturbed energy (eV) against energy level (n).

Table 1. Wave functions of the hydrogen-like atom for $n = 1, 2, 3$. $r \in [0, \infty]$, $\phi \in [0, 2\pi]$, $\theta \in [0, \pi]$.

n	l	m	Wave function $\psi_{nlm}(r, \theta, \phi)$
1	0	0	$\frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$
2	0	0	$\frac{1}{4\sqrt{2\pi a_0^3}} \left(2 - \frac{r}{a_0}\right) e^{-r/2a_0}$
2	1	0	$\frac{1}{4\sqrt{2\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \cos\theta$
2	1	±1	$\frac{1}{8\sqrt{\pi a_0^3}} \frac{r}{a_0} e^{-r/2a_0} \sin\theta\, e^{\pm i\phi}$
3	0	0	$\frac{1}{81\sqrt{3\pi a_0^3}} \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right) e^{-r/3a_0}$
3	1	0	$\frac{1}{81\sqrt{3\pi a_0^3}} \left(6 - \frac{r}{a_0}\right) \frac{r}{a_0} e^{-r/3a_0} \cos\theta$

where $E_n^{(0)}$ is the unperturbed energy, R is the Rydberg's constant = 13.6 eV and $E_n^{(1)}$ is the first order correction to the shift energy. The perturbation or dipole moment is given by

$$H' = q \cdot r\,, \tag{7}$$

$$E_n^{(1)} = \left\langle \Phi_{(r,\theta,\phi)} \left| H' \right| \Phi_{(r,\theta,\phi)} \right\rangle, \tag{8}$$

where the constants: $Z = 1$, $a_0 = 529\ fm$, $\pi = 3.142$, $q = e = 1.6 \times 10^{-19}\ C$. The energy shifts to the eigen states are computed viz:

$$E_{100}^{(1)} = \frac{e}{\pi a_0^3} \int_0^\infty r e^{-2r/a_0}\, dr\,, \tag{9}$$

$$E_{200}^{(1)} = \frac{e}{32\pi a_0^3} \int_0^\infty r \left(2 - \frac{r}{a_0}\right)^2 e^{-r/a_0}\, dr\,, \tag{10}$$

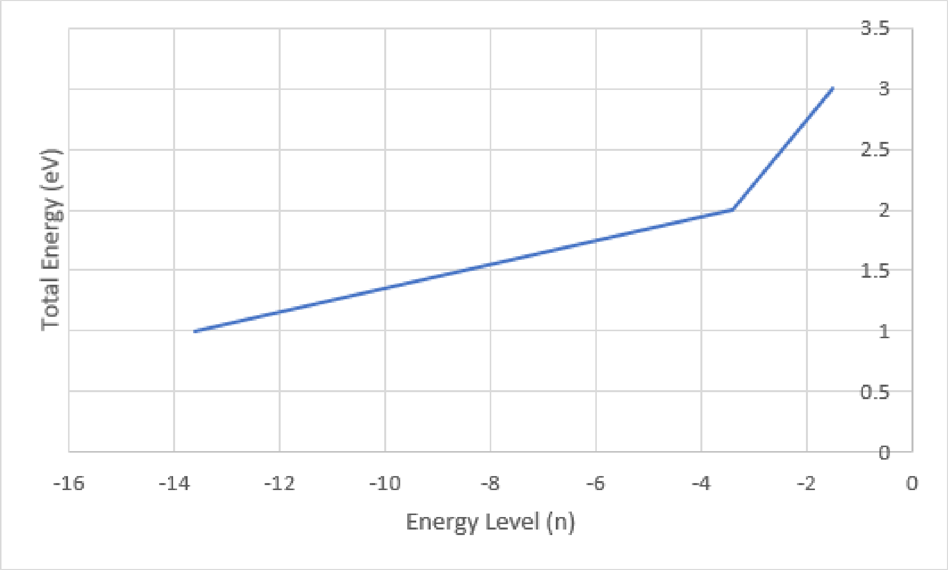

Figure 2. Total energy (eV) against energy level (n).

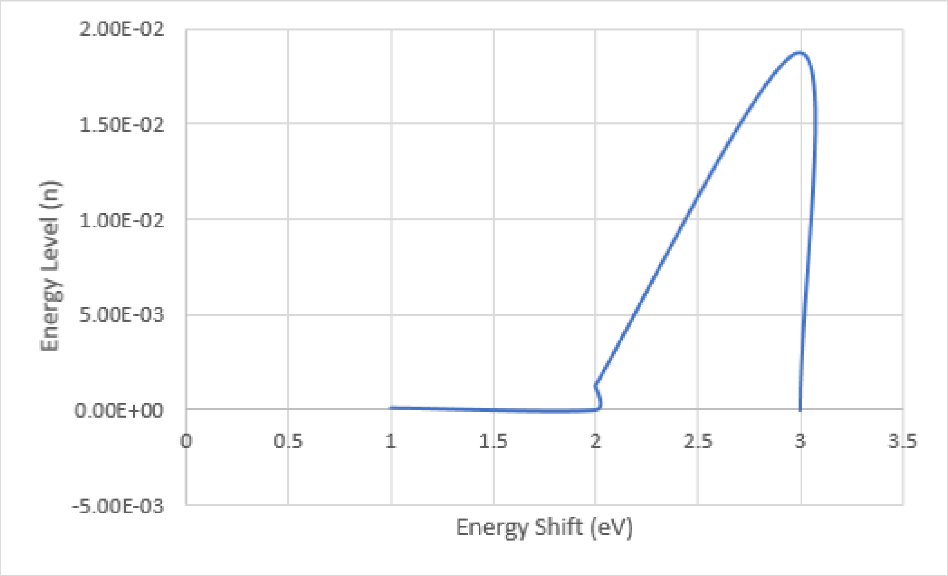

Figure 3. Energy level (n) against energy shift (eV).

$$E^{(1)}_{210} = \frac{e}{32\pi a_0^5} \int_0^{\infty} r^3 e^{-r/a_0}\, dr \int_0^{\pi} \cos^2\theta\, d\theta\,, \tag{11}$$

$$E^{(1)}_{211} = \frac{e}{192\pi a_0^5} \int_0^{\infty} r^3 e^{-r/a_0}\, dr \int_0^{\pi} \sin^3\theta\, d\theta \int_0^{2\pi} d\phi\,, \tag{12}$$

$$E^{(1)}_{21-1} = \frac{e}{192\pi a_0^5} \int_0^{\infty} r^3 e^{-r/a_0}\, dr \int_0^{\pi} \sin^3\theta\, d\theta \int_0^{2\pi} d\phi\,, \tag{13}$$

$$E^{(1)}_{300} = \frac{e}{19683\pi a_0^5} \int_0^{\infty} r \left(27 - 18\frac{r}{a_0} + 2\frac{r^2}{a_0^2}\right)^2 e^{-r/a_0}\, dr\,, \tag{14}$$

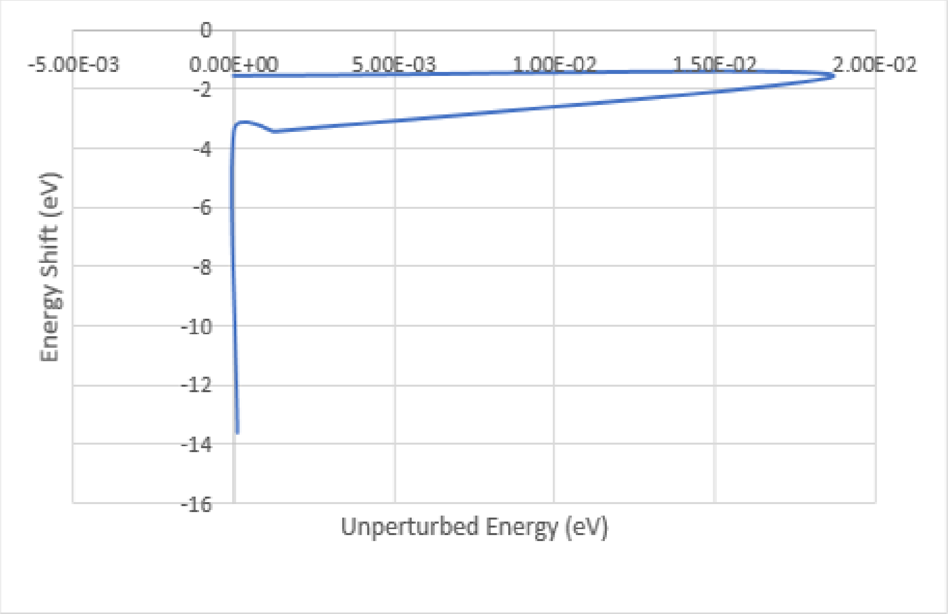

Figure 4. Energy system specific curve for energy shift (eV) against unperturbed energy (eV).

and

$$E_{310}^{(1)} = \frac{e}{19683\pi a_0^5}\int_0^{\infty} r^3 e^{-r/a_0}\,dr \int_0^{\pi} \cos^2\theta\,d\theta\,. \tag{15}$$

Numerically, the integrals equations (9) to (15) are evaluated by the method of trapezoidal rule using MATLAB software. In order to evaluate a definite integral,

$$I = \int_a^b f(r)\,dr,$$

the following expression for trapezoidal rule was applied:

$$I = \frac{h}{2}\left[f(a) + 2\left(f(r_1) + f(r_2) + f(r_3) + \cdots + f(r_{n-1})\right) + f(b)\right], \tag{16}$$

where $a = r_0$, $b = r_n$, and $h = \frac{b-a}{n}$ is the width of the strips.

3. Result and discussions

The computed energy shifts in the different eigen states of the Hydrogen atom are presented in Table 2. Demonstrating how the wave function of hydrogen atom exhibits degeneracy, especially $n = 2,\ n = 3$ states. This implies that $n = 2,\ n = 3$, have different states but the same energy as a result of the subshells with angular momentum l, which contains $2l + 1$ distinct state corresponding to positive value of m (magnetic angular momentum quantum number) $m = -l \pm 1$. The total degeneracy of the energy levels n is caused given by n^2 .

In the hydrogen atom, the dipole moment is the product of the charged proton (e) and perpendicular distance between proton and electron in its orbit (r). Thus, as the orientation of the electron charges (θ, ϕ) change, the dipole moment also changes and thus has a perturbing effect on the energy levels of the hydrogen atom leading to a shift in its energy. This is confirmed in Table 2, as it can be seen that the energy shift which increases the energy of the atom slightly from the ground state energy function Φ_{100} to the second exicted state Φ_{300}, while the degeneracy state Φ_{310} and above experiences infinitesemal energy shift. This is because the probability of the electron found in the lower energy level is greater than higher energy level and so it is mostly affected there by energy shift. Also, the dipole moment could increase liberational energy of the atom and thus lead to more excitement even though its impact is quite negative.

Figure 1 is a plot of unperturbed energy against energy level which appears as a series of positive straight lines on an energy level diagram. The vertical axis represents energy, and the horizontal line represents a discrete energy level. For an unperturbed state, this diagram represents the ideal system, before any external electric fields or interactions (perturbations) are applied. As the perturbation is introduced, these levels shift into new perturbed energy levels which is shown as a separate in the direction of line or curve on an

Table 2. Energy shift due to dipole moment in hydrogen-like atom.

(n)	ψ_{nlm}	$E_n^{(0)} = -13.6/n^2$ (eV)	$E_n^{(1)}$ (eV)	$E_n = E_n^{(0)} + E_n^{(1)}$ (eV)
1	ψ_{100}	-13.60	1.34028×10^{-4}	-13.5999
2	ψ_{200}	-3.400	1.21570×10^{-5}	-3.39999
2	ψ_{210}	-3.400	1.25559×10^{-3}	-3.39874
2	$\psi_{21\pm1}$	-3.400	1.31485×10^{-3}	-3.39869
3	ψ_{300}	-1.511	1.87278×10^{-7}	-1.49227
3	ψ_{310}	-1.511	8.72096×10^{-169}	-1.511

expanded diagram. This is exactly the same as Figure 2 when the total energy is plotted against energy level. In essence, the plots in Figure 1 are energy level diagram where the unperturbed energies are the reference points from which perturbations cause shifts. Figure 3 is a plot of energy level against energy shift which is generally referred to as an energy level diagram or Energy shift curve. The shift (difference in energy) corresponds to the energy absorbed from the external field or simply shows how energy levels shift in response to an external field. The energy shift at point 1eV to 2eV is constant with quantized energy levels in electron volts and increases at point 2eV then degenerates at 3eV. This visualizes how energy is stored, transferred, or changes in a system, and the ”energy shift” is the difference or change between these levels or states.

Figure 4 is a plot of energy shift against unperturbed energy which generally shows a system-specific, often non-linear curve. The specific nature of the plot depends heavily on the particular physical system and the type of perturbation applied. This is typically plotted as a function of the perturbation strength parameter, λ, to show how they evolve from the unperturbed ground state values to the full perturbed values. It visualizes the effect of a specific perturbation on the entire energy spectrum of a system, highlighting phenomena like shifts.

4. Conclusion

Numerical evaluation of energy shifts due to dipole moments interaction in a hydrogen atom was carried out, significantly in understanding fine details of atomic behavior and contributing to various scientific disciplines. The research involved applying perturbation theory and numerical techniques to quantify the changes in energy levels due to dipole orientations and magnitudes, contributing to a deeper understanding of atomic behavior and its implications in various scientific disciplines, considering the dipole moment's effect on the hydrogen atom's energy levels, and exploring the resulting changes in spectral characteristics. The outcomes of this research could have implications in precision measurements, quantum computing, and the understanding of complex atomic systems. The study's objectives include quantifying dipole moment interaction, understanding perturbation theory, deriving mathematical expressions, analyzing spectral changes, and validating numerical results through comparison with theoretical predictions and experimental observations. The study's scope involves investigating the impact on energy levels, considering various dipole orientations and magnitudes. Overall, it is found that as the orientation of the electron charges (θ, ϕ) change the dipole moment also changes and thus has a perturbing effect on the energy levels of the hydrogen atom leading to a shift in its energy.

For further studies on numerical evaluation of energy shifts due to dipole moment interactions in a hydrogen atom, we recommend that data about how electron density redistributes during atomic and molecular interactions; accurate calculation of interaction-induced dipoles, such as those in hydrogen-hydrogen or hydrogen-nitrogen collisions, which is vital for interpreting collision-induced absorption (CIA) phenomena, precise numerical methods for calculating energy shifts in atomic systems that contribute to the development and validation of theoretical models for complex quantum mechanical problems, the study of hydrogen atoms under various conditions, such as confinement within spatial boundaries or immersion in dense plasmas which is crucial for modeling high-temperature propulsion devices, fusion energy research, and astrophysical plasmas, the need for accurate and efficient numerical simulations that drives the development of advanced computational chemistry methods, such as coupled-cluster calculations and machine learning potentials for electric field responses, and above all the accurate theoretical predictions of energy shifts that are crucial for interpreting experimental results from high-resolution spectroscopy and for ongoing searches for new physics beyond the Standard Model such as measuring the electric dipole moment of the electron in heavy polar molecules should be taking into consideration.

Data availability

No new data were generated or analyzed in this study.

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